

# PATENT SPECIFICATION

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## (54) ANTI-FOULING PAINT

(71) We, CENTRE NATIONAL POUR L'EXPLOITATION DES OCEANS an organisation of the Government of France, of 66, Avenue d'Iena, 75116-Paris, FRANCE, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The invention relates to an anti-fouling paint containing at least one toxic substance.

As is known, an anti-fouling paint is one which is intended to be applied to the hulls of ships or to the surface of any other immersed object, usually on to a coating of rust-resistance paint, for the purpose of preventing the fixation on to the surface of a certain marine fauna and a certain marine flora, comprising for example algae, shellfish, molluscs and corals.

Several types of anti-fouling paints are known.

Certain anti-fouling paints operate by exfoliation, i.e. by periodically flaking off, the flakes carrying away the marine organisms fixed on the surface of the paint flakes.

However, most of the anti-fouling paints operate by progressive liberation of toxic substances, the purpose of which is to destroy the marine organisms coming into contact with the hull or at least to inhibit their fixation to the hull.

In this last type of anti-fouling paint, the liberation of the toxic substance results from the leaching out or release of this substance by the sea water, this being a phenomenon which is produced just as well when the ship is moving as when it is stationary. Certain toxic pigments, such as cuprous oxide, even have a higher leaching out speed when the ship is in motion than when it is stationary.

Now the tendency for the fouling organisms to become fixed to the surface only exists in practice when the hull is stationary in relation to the surrounding mass of water. It is thus pointless for the toxic substance to be liberated while the ship is under way, since this results in a waste of the substance and a premature loss of efficiency of the anti-fouling paint.

With the object of increasing the length of time when an anti-fouling paint is active, it has been proposed in French Patent No. 2,155,166 to seal the toxic product inside microcapsules which have a water-soluble casing formed from gelatine, nitrocellulose or methylcellulose, the diameter of the capsules being from 5 to 30 microns and the thickness of its casing being from 3 to 10 microns, these microcapsules being dispersed in a proportion which is between 5 and 25 % in the binding agent or vehicle of the paint.

According to this patent, the liberation of the toxic product sealed in the microcapsule can take place by various procedures, namely, either by osmosis through the wall, or by dissolution of the wall, or by bursting of the wall under the action of a blowing agent or under the mechanical action produced by brushing.

In order to regulate the release of the toxic product in time, thereby stabilising its diffusion, it is mentioned in the patent that it is possible for the toxic agent to be incorporated into the microcapsule in admixture with a resin having the property of being polymerised under the action of humidity.

The process described in the aforementioned patent enables the speed of release of the

toxic substance to be slowed down or regulated to a certain degree, but it does not however permit of avoiding the leaching out of this substance while the ship is under way.

The object of the present invention is specifically to provide an anti-fouling paint having the property of only releasing the toxic substances in the presence of the marine organisms which it is desired to inhibit.

To this end, the anti-fouling paint according to the invention has the toxic substance incorporated uniformly in a discontinuous solid matrix which is insoluble in sea water and is dispersed in the paint, this matrix being at least partly formed from at least one substance which dissolves in sea water under the action of enzymes liberated by the marine organisms which it is desired to inhibit and/or by bacterial action resulting from a film of marine bacteria in contact with the surface of the paint.

Thus, in the anti-fouling paint according to the invention, the toxic substance is not sealed inside microcapsules, as in the case which is described in the aforementioned French patent, but is homogeneously incorporated in a solid matrix of which it forms an integral part.

As a consequence, instead of being brought more or less suddenly into contact with the marine medium and the fouling agents after the wall of the micro-capsule has been dissolved or broken, as is the case with the aforementioned French patent, the toxic substance is liberated, in accordance with the present invention, in proportion with the dissolving of the matrix in which it is incorporated.

However, since this matrix is formed by a solid substance which dissolves in sea water under the action of enzymes liberated by the marine organisms which it is desired to inhibit, or by the bacterial film in contact with the surface of the paint, the dissolving of the matrix, and the simultaneous release of the toxic substance which flows gently therefrom, take place only when this is necessary, i.e. in the presence of the marine organisms and/or the bacterial film, i.e. when the speed of displacement of the substrate covered with the anti-fouling paint relative to the sea water is zero or at least sufficiently low for these organisms to become fixed on the substrate. The marine organisms may thus be the cause of their own destruction.

The solubilisation of the matrix which contains the toxic substance may also be caused by enzymes liberated by the bacterial film in contact with the surface of the anti-fouling paint.

As is known, such a bacterial film is formed by a flora of microorganisms which proliferate in the liquid layer which is in the immediate vicinity of the surface of the immersed body, that is to say, in a layer having a thickness of the order of a few microns from the surface.

The presence of this bacterial film contributes to a large degree to the fixation of the vegetable or animal fouling media on the surface of the immersed body, because this film preferably constitutes nutritive medium for the fouling media, which as a consequence have a tendency to be drawn towards it.

This is the reason why the destruction of the bacterial film as a consequence of the liberation of a toxic substance by the anti-fouling paint also contributes to the inhibition of the fixation of the fouling media.

On the other hand, the triggering of the mechanism for liberating the toxic substance under the effect of enzymes originating from the bacterial film permits the inhibition of the fixation of marine organisms which would, in themselves, be incapable of liberating enzymes having an action for making the matrix soluble, this seeming to be, for example, the case with certain algae.

It is probable that the liberation of the toxic substance by the anti-fouling paint in accordance with the invention results, in practice, from the combination of the action of enzymes originating from the organisms which it is desired to inhibit and the action of enzymes originating from the bacterial film.

Consequently, the invention permits a best possible utilisation of the toxic substance contained in the anti fouling paint, the result of which is a considerable increase in the time during which this paint is effective under normal operating conditions (i.e. in the case where the substrate covered by the anti-fouling paint is subjected to a normal alternation of periods during which the marine organisms have a tendency to become fixed on the substrate, as when a ship is stationary in a port, and periods during which this tendency does not exist or is not very considerable, such as when a ship or vessel is travelling at high speed).

Examples of suitable toxic substances are toxic pigments, such as cuprous oxide ( $\text{Cu}_2\text{O}$ ), monomeric or polymeric organometallic derivatives of tin, such as tributyl-tin oxide (TBTO), tributyl-tin acetate (TBTA) and tributyl-tin fluoride (TBTF).

Bearing in mind that the marine organisms which it is desired to inhibit are: herbivorous organisms such as the shellfish, oysters and mussels, which secrete enzymes capable of degrading the polysaccharides: cellulases, alginases; carnivorous organisms such as barnacles, which secrete enzymes capable of degrading proteins: proteases, esterases; omnivorous organisms, such as the ascidiae, bryozoeae, small size barnacles, serpulae, which secrete all the previously indicated enzymes;

and that the bacterial film close to the immersed body is formed essentially by microorgan-

isms which excrete cellulases, amylases, proteases and esterases, it is easily possible to determine the type of matrix which can be used. Thus, the matrix which is used in the paints according to the present invention is preferably formed from at least one biodegradable compound which is insoluble or is only slightly soluble in sea water, selected from: proteins, polysaccharides, polyesters, polyurethanes, celluloses and their derivatives and particularly

gels or regenerated cellulose and gels of protein, such as coagulated albumin. Preferably, the solid matrix in which the toxic substance is incorporated is in the form of fine powder particles which are obtained, for example, by grinding particles or granules of larger dimension or a single compact mass. Preferably, the grain size of this fine powder is not greater than 100 microns.

Preferred matrix-forming material is, for example, regenerated cellulose gel or a coagulated protein gel.

As regards the proportion of solid matrix containing the toxic substance in the paint, as well as the final content of toxic substance in the paint film, these are dependent on the nature of the matrix and also on the nature of the toxic substance.

Generally speaking, the mixture of matrix and toxic substance contains from 5 to 50% by weight of toxic substance; the assembly of matrix and toxic substance is generally present in an amount of from 20 to 60 parts by weight to 100 parts by weight of paint, including solvent.

For example, in the case where the solid matrix is formed by an albumina gel and where the toxic substance is tributyl-tin fluoride (TBTF), the optimal proportion of albumina gel in the paint is between 20 and 60% by weight, based on the total weight of the paint, and the optimal content of TBTF in the film of paint obtained after the paint has been applied to a substrate and the film has dried, is between 10 and 30% by weight, based on the weight of the film of dry paint.

The paintbase compositions for forming the anti-fouling paints are known to the person skilled in the art and they are generally formed from:

film-forming resin (Vinylite Vyhh

"Vinylite" is a Registered Trade Mark)

5 - 20 %

pore-forming resin (Colophony)

5 - 20 %

plasticiser (tricresyl phosphate)

2 - 8 %

diluent methyl isobutylketone

40 - 70 %

solvent

0 - 30 %

xylene

It is quite obvious that it is possible in these paints to use other insoluble film-forming resins of the vinyl, alkyd, urethane, acrylonitrile, acrylate, epoxy and chlorinated elastomer type.

It is also possible to employ other pore-forming agents, such as the soluble polymers:

-polyvinyl alcohol

-polyacrylamides

-polyacrylic and polymethacrylic acids

-cellulose derivatives (methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose)

-oxides of polyethylene and polyethylene imines

-polyvinyl pyrrolidone;

or biodegradable polymers such as:

-starch derivatives

-aliphatic polyester resins

-hydrolysable opolyurethanes.

Certain plasticisers may also serve as pore-forming agents, for example, esters of fatty acids.

It is to be noted that, in addition to the aforementioned advantage of having a long period of action, the anti-fouling paint according to the invention provides the additional advantage of limiting to a large degree the danger of intoxication or poisoning during storage, handling and application of the paint, due to the fact that the toxic substance is not in its free state, but is incorporated into a matrix.

The invention is illustrated by the following Examples:

#### Example 1

a) Preparation of filled microspheres of coagulated albumin gel containing particles of cuprous oxide powder ( $\text{Cu}_2\text{O}$ ) in the form of a homogeneous dispersion.

Into a three-necked 1-litre spherical flask equipped with glass mechanical stirrer device were introduced 900 millilitres of Vaseline petroleum jelly ("Vaseline" is a Registered Trade Mark). (FH; Swiss pharmacopeia), i.e. 730 grams.

Thereafter, the "Vaseline" had progressively dispersed therein, while stirring and at ambient temperature, a mixture of an aqueous 15 % by weight albumin solution and cuprous oxide ( $\text{Cu}_2\text{O}$ ) as a fine powder (wetted prior to mixing with the albumin solution), the proportion of cuprous oxide in this mixture being 2 % by weight, based on the weight of the albumin solution.

Globules of albumin containing the cuprous oxide powder were formed within the "Vas-

eline" mass at ambient temperature.

The temperature of the contents of the flask was then slowly and progressively raised to 120°C, while continuing the vigorous agitation thereof. As soon as this latter temperature was reached (the albumin globules were then transformed into solid microspheres of coagulated albumin gel), the heating was stopped and the temperature of the contents of the spherical flask allowed to fall to 40°C, while stirring well.

The stirring was then stopped, the microspheres of albumin gel separated from the "Vaseline" by decantation and then carefully washed with petroleum ether, and then with acetone (this alternate washing procedure is repeated three times) and, finally, with ethyl ether.

In this way, microspheres of coagulated albumin gel were obtained, forming a solid matrix containing fine powder particles of cuprous oxide dispersed homogeneously in the matrix. The diameter of the said microspheres was slightly smaller than 100 microns.

b) *Preparation of an anti-fouling paint*

These microspheres were crushed so as to reduce them to a fine powder, which was washed with acetone and then with methanol, and finally with ether. After this operation, the powder thus obtained was dried and homogeneously dispersed in a paint composition (mixture of vehicle diluent and solvent which also contains tricresyl phosphate) having the following composition: (as percentages by weight):

vinyl film-forming synthetic resin

("Vinylite" Vyhh\*)

12.30

colophony resin

12.30

tricresyl phosphate

4.60

methyl isobutyl ketone

42.30

xylene

28.50

(\*) "Vinylite" Vyhh: product manufactured by Union Carbide, (vinyl chloride - vinyl acetate copolymer having a mean molecular weight).

The proportion of coagulated albumin gel powder which was added to the composition as specified above was 40% by weight, based on the weight of this composition.

In this way, an anti-fouling paint was obtained which led to the release of the toxic pigment (cuprous oxide) in the presence of marine, vegetable or animal organisms, which excrete at least one proteolytic enzyme, such as trypsin, capable of solubilising the particles of coagulated albumin gel covering the toxic pigment.

The release ceases in the absence of enzyme, and starts again as soon as such an enzyme is present.

*Example 2*

a) *Preparation of a coagulated albumin gel containing tributyl-tin oxide (TBTO) as toxic substance*

12 volumes of an aqueous solution of albumin with 15 % by weight of albumin were mixed while stirring and at ambient temperature with 4 volumes of a solution of tributyl-tin oxide in methanol (containing about 1000 g of TBTO per litre of methanol). A voluminous precipitate of partially coagulated albumin gel was formed, and this was heated to 70°C so that it was completely coagulated. The coagulated albumin gel as thus obtained contains in uniformly dispersed form a quantity of TBTO corresponding to half the total weight of albumin plus TBTO.

b) *Preparation of an anti-fouling paint*

The coagulated albumin gel obtained as described above was reduced to a fine powder and homogeneously incorporated into a paint composition which was identical with that which is described in Example 1, at the rate of 50% by weight of albumin gel relatively to the weight of the said composition.

In this way, an anti-fouling paint was obtained which includes a total quantity of 31.55% by weight of tributyl-tin oxide (TBTO) after a paint film has been formed on a substrate.

This film contains 23.68% by weight of TBTO (relatively to the total weight of the film after the latter has been dried at 50°C, under vacuum), incorporated into the coagulated albumin gel, the remainder being in a free form.

This paint film also releases the toxic product (TBTO) in the presence of marine organisms which excrete proteolytic enzymes acting on the albumin gel.

*Example 3*

As for Example 2, but only 12% by weight of albumin gel were incorporated into the paint composition.

The anti-fouling paint film contained a total quantity of 14.66% by weight of TBTO, the content of TBTO incorporated in the albumin gel being 11 % by weight, based on the total weight of the dry paint film (after drying under vacuum at 50°C).

*Example 4*

As for Example 2, but using tributyl-tin acetate (TBTA) as toxic substance.

Proportion of albumin gel incorporated into the paint composition: 64 % by weight.

Total quantity of TBTA in the paint film immediately after this latter has been formed: 34.32 % by weight.

Quantity of TBTA incorporated into the albumin gel (content of TBTA in the film after drying at 50°C under vacuum): 17.74% by weight.

#### Example 5

As for Example 4, but with the following proportions of TBTA:

Proportion of albumin gel incorporated into the paint composition: 24% by weight.

Total quantity of TBTA in the paint film immediately after this latter has been formed: 22.66% by weight.

Quantity of TBTA incorporated into the albumin gel (content of TBTA in the film after drying at 50°C under vacuum): 11.71 % by weight.

Plates or sheets of polyvinyl chloride, coated on one face with films of anti-fouling paints prepared as indicated in Examples 2 to 5 were kept immersed for 100 days in the sea, during Summer months, in a temperature region (the Brest Roads, France), as a test for the effectiveness of these paints.

Prior to the tests, the paint films were subjected to drying under vacuum, at 50°C, so as to eliminate the fraction of organic tin derivative not incorporated into the matrix of coagulated albumin gel.

After the test, the surfaces of the polyvinyl chloride sheets covered with the films of anti-fouling paint were completely free from any traces of fouling, whereas the opposite faces, not covered with anti-fouling paint, were on the contrary heavily loaded with fouling media (essentially shellfish) which are solidly fixed on the surface of the said sheet.

The following table sets out the results of this test.

Test sample	Ex.4	Ex.5	Ex.2	Ex.3
% albumin gel + organo-tin in the paint	64	24	50	12
Albumin organo-tin ratio	1/1	1/1	1/1	1/1
Before tests				
Weight of paint (g/m <sup>2</sup> )	116	38	100	50
% of tin	6.04	3.98	9.44	4.38
Weight of tin/g/m <sup>2</sup> )	7	1.51	9.44	2.19
After tests				
Weight of paint (g/m <sup>2</sup> )	38.2	24.8	22.2	28.9
% of tin	2.1	2.46	2.33	1.73
Weight of tin (g/m <sup>2</sup> )	0.8	0.61	0.51	0.49
Total tin loss (g/m <sup>2</sup> )	6.2	0.90	8.93	1.7
Tin loss in µg/cm <sup>2</sup> /day	6.2	0.90	8.93	1.7
Theoretical active life (days)	113	167	106	129

This test accordingly illustrates the perfect efficiency of the anti-fouling paints prepared in the manner as described in Examples 2 to 5. It is to be noted that this efficiency is obtained with a speed of release of toxic substance, in respect of the compositions of Examples 3 and 5, which is much lower than the speeds of release which are necessary in the case of the known anti-fouling paints, in which the toxic substance is also selected from TBTO and TBTA, namely, at least 4 micrograms of tin/cm<sup>2</sup>/day.

#### Example 6

As for Example 2, but using tributyl-tin fluoride (TBTF) in methanol at 50°C as toxic substance.

The proportion of albumin gel incorporated into the paint composition is 40 % by weight.

The total quantity of TBTF in the paint film after the latter has been formed is 20% by weight.

#### Example 7

As for Example 2, but using triphenyl-tin fluoride (TPhTF) as toxic substance.

The proportion of albumin gel is 45 % by weight of the paint after the film has been formed and the quantity of TPhTF is 20 % by weight of the paint.

#### Example 8

As for Example 2, but, after having reduced the albumin gel to powder, the powder was obtained was washed with a mixture comprising equal volumes of water and methanol in order to eliminate the fraction of TBTO liberated from the albumin gel at the time of the crushing or grinding operation.

An anti-fouling paint was obtained which is practically free from any toxicity while it was

being stored, handled and applied.

WHAT WE CLAIM IS:-

1. An anti-fouling paint for inhibiting the fixation of marine organisms on substrates which are immersed in sea water and including at least one toxic substance, wherein the toxic substance is uniformly incorporated into a discontinuous solid matrix which is insoluble in sea water and is dispersed in the paint, said matrix being at least partially formed from at least one substance which can be dissolved in the sea water under the action of enzymes liberated by the marine organisms which it is desired to inhibit and/or by bacterial action resulting from a film of marine bacteria in contact with the surface of the paint.
2. An anti-fouling paint as claimed in Claim 1, wherein the matrix is formed from at least one biodegradable compound which is insoluble or only slightly soluble in sea water, selected from proteins, polysaccharides, polyesters, polyurethanes, cellulose and their derivatives.
3. An anti-fouling paint as claimed in Claim 1, wherein the matrix is formed from a gel of regenerated cellulose.
4. An anti-fouling paint as claimed in Claim 1, wherein the matrix is formed from a gel of coagulated protein.
5. An anti-fouling paint as claimed in any of Claims 1 to 4, wherein the matrix is in the form of powder particles having a grain size at most equal to 100 microns.
6. An anti-fouling paint as claimed in any of Claims 1 to 5, wherein the mixture comprising matrix and toxic substance contains from 5 to 50 % by weight of toxic substance.
7. An anti-fouling paint as claimed in any of Claims 1 to 6, wherein the mixture of matrix plus toxic substance represents from 20 to 60 parts by weight to 100 parts by weight of paint.
8. An anti-fouling paint as claimed in any of the preceding claims, wherein the toxic substance is cuprous oxide or monomeric or polymeric organo-tin compounds.
9. An anti-fouling paint substantially as described with reference to the Examples.

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